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Abstract of the Disclosure

In the electrolytic refining or winning of copper, high purity copper is deposited directly upon reusable, plate-like, relatively rigid, edge-masked cathode blanks in deposits which are relatively heavy. After deposition the deposited copper is stripped from the cathode blank for melting. The thin copper cathode starting sheets commonly employed in the electrodeposition of copper are dispensed with entirely.

This invention is directed to an improved process for the electrolytic recovery of copper, including electro-refining and electrowinning.

Electrolytic processing may be used in purifying partially refined copper or in winning copper from acid copper-bearing solutions including solutions produced by leaching copper ores. In the electrolytic refining process, the anode is composed of crude (partially refined) copper and high purity copper is deposited on the cathode. In the electrowinning of copper, the anode is composed of an insoluble metal and is immersed in an electrolyte containing dissolved copper. High purity copper is deposited on the cathode and fresh copper-rich electrolyte is introduced to replace that depleted in copper. In the description of these processes which follows below, electrolytic refining is first described.

Blister copper, as produced by the copper converter contains close to 99% copper. In order to satisfy the demands of industry for an exceedingly pure grade of copper, this blister copper is further refined to remove impurities by a process including electrolytic refining. The blister copper is first melted in a reverberatory furnace for casting into crude copper anodes. This melting, which is not primarily intended to effect additional purification, nevertheless does usually result in the removal of oxygen and sulfur so that the crude copper anodes have a copper content usually in excess of 99%. The electrolytic refining of the crude copper anodes which follows, further purifies the copper so that the product of the electrolytic refining step has a copper content of more than about 99.9%.



As the electrolytic refining process is presently practiced, in the almost universally used "multiple process", the copper is deposited upon thin sheets of high purity copper, known as cathode starting sheets, which are electrically connected in parallel. These cathode starting sheets are produced, in a separate operation, in an electrolytic cell. In that cell, copper is deposited for a period, usually not exceeding about 24 hours, on rigid mother blanks of rolled copper provided with a thin coat of oil or other parting film thereon. The thin copper sheets thus deposited are stripped manually from the blanks, this operation being facilitated by the parting film on the blanks which reduces adherence of the deposit. A proportion of these thin sheets, usually one in four to one in ten, are cut up and joined to full cathode sheets as electrically conducting supporting loops for the cathodes. The cathode starting sheets, which have a thickness of perhaps 0.02 or 0.035 inch, and weigh generally less than 15 to 20 pounds, must first be straightened. The straightened cathode starting sheets are hung by the loops on a contact rod (hanger bar) and positioned between crude copper anodes in a commercial electrolytic refining cell. Upon these flimsy and readily distorted cathode starting sheets, all subsequent high purity copper is deposited as the anodes are gradually dissolved and thereby consumed. In the course of electrolytic deposition upon the starting sheets, warpage often occurs, and removal of the warped cathodes from the bath for an additional straightening (flopping) operation is required to forestall a short circuit contact between the warped cathodes and the anodes. Continual difficulties are encountered in maintaining electrical contact to the light starting sheet assemblies.

After completion of the deposition stage, which may take as much as ten days, or more, the cathodes will have a thickness of as much as 1/2 inch or more. These cathodes are then melted into ingot or bar or other suitable form of high purity copper.

10 The multiple electrolytic process for electrowinning copper, which has just been outlined, has been in commercial use for at least 100 years without major change in the over-all process, although innumerable improvements have been made in various details of the process and in the apparatus employed, over the years. Each year sees additional proposals made for improving the process with a substantial amount of attention devoted to improving operations in connection with production of the cathode starting sheets (for example, see Canadian Patent Nos. 708,933 and 741,314, issued May 4, 1965 and August 23, 1966, respectively). However, despite this activity in the field it is not evident that similar thought and effort have been expended to entirely eliminate the troublesome starting sheets and the expensive, tedious operations associated therewith.

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It will be apparent that there is a large component of manual labor inherent in the multiple copper refining process. It has been calculated for one electrowinning plant, that over 60% of the tank house labor is devoted to cathode starting sheets (stripping, looping, riveting, sheet flopping and the subsequent tending during plating). It is evident that if the costly operations involved in producing and handling cathode starting sheets can be eliminated, great savings in time, manpower and plant can be effected.

30 It has further been found that a substantial amount

of electrolyte becomes entrapped during the electrolytic process at the joints between the loops and the starting sheets. This entrapped electrolyte introduces sulfur and other impurities into the ingot or bar obtained upon melting and casting of the electrolytic copper, thereby limiting the level of purity which can be attained. Also, the warping of the starting sheets obviously results in non-uniform spacing between anodes and cathodes and a consequent lack of current uniformity. This non-uniform current distribution results in the formation of
10 nodules and coarse striations on the cathode which occlude electrolyte with its soluble impurities. Thus, the purity of the copper produced would be materially enhanced by elimination of these several sources of contamination inherent in utilizing cathode starting sheets.

In the electrowinning of copper, the operation closely resembles electrolytic refining, including the use of cathode starting sheets, but an insoluble anode (antimonial lead, for example) is employed instead of a copper anode, and the electrolyte is the source of the copper deposited on the
20 cathode starting sheet. The copper present in the electrolyte may be provided by leaching copper ores with a sulfuric acid solution and fresh electrolyte is advantageously introduced into the electrolytic cell during deposition as the original electrolyte becomes depleted in copper and is removed.

It has now been discovered, in a process for electro-deposition of copper, which may be either electrorefining or electrowinning, that heavy deposits of high purity copper may be produced directly on suitable cathode structures, thereby eliminating the necessity for the production and utilization
30 of copper starting sheets.

It is an object of the invention to provide an electrolytic process in which heavy deposits of high purity copper are made directly upon sturdy relatively rigid, reusable cathode blanks without employing intermediate cathode starting sheets.

It is a further object of the invention to provide an electrolytic refining process in which copper cathode starting sheets are not required.

10 It is another object of the invention to provide an electrowinning process in which copper cathode starting sheets are not required.

It is still another object of this invention to provide a sturdy, reusable, relatively rigid, masked cathode structure suitable for receiving direct deposition of heavy, high purity copper deposits.

Other objects and advantages of the invention will become apparent from the following description taken in conjunction with accompanying drawings in which:

20 Fig. 1 shows a side elevation view of a cathode structure suitable for the practice of the invention.

Fig. 2 is a cross-sectional view of an insulating member mounted on the edge of the cathode taken along line 2-2 of Fig. 1.

Fig. 3 is a cross-sectional view of the bottom edge of the cathode of Fig. 1 taken along line 3-3 of Fig. 1.

30 Generally speaking, the invention is based on the discovery that electrolytic refining or winning of copper can be carried out in a manner such that copper of high purity is deposited directly upon reusable, plate-like, relatively rigid, edge-masked cathode blanks, in deposits which are

relatively heavy, and which can thereafter be stripped from the cathode and melted. In this process a cathode starting sheet as required in the prior art, is not only unnecessary, it is not, in fact, even useful and is dispensed with entirely.

More particularly, in the process of the invention, copper is electrolytically deposited upon suitable, relatively rigid, cathode blanks for a period (usually at least about 100 hours) sufficient to attain a deposit thickness of at least 1/8 inch of copper on each side of the blanks, e.g., a deposit weight of at least 5 pounds per square foot of surface area on each cathode. The surface roughness of the cathode blanks is sufficient to achieve limited adherence of the deposited copper to the blank surfaces, and the cathode blanks are provided with insulation which completely covers the side edges thereof to prevent deposition of copper on the side edges thereby facilitating stripping. The electrolyte employed in the process contains from about 30 to 100 grams per liter of copper and from about 50 to 250 grams per liter of sulfuric acid. The bath is maintained at a temperature in the range from about 40° to 70°C. (104° to 158°F.) and the cathode current density is in the range of from about 15 to 35 amperes per square foot. After the deposition step is completed, the deposited copper is stripped from the cathode blank and removed for melting and the cathode blanks are returned to an electrolytic cell for further deposition of copper.

Referring now to Figs. 1 through 3 of the drawing, it will be seen that in the cathode structure 20, the plate-like cathode blank 10 is provided with lugs 11 at the top thereof. The lugs are attached to the conductor bar 12 by appropriate fastening means 13 such as, for example, rivets or bolts. The bottom edge 16 of the cathode blank 10 is provided

with an inverted V-shaped groove 18 leading substantially to the cathode blank faces. The side edges 14 and marginal portions 15 of the cathode blank 10 have mounted thereon insulating masking channel members 25. The bottom walls 26, and the side walls 27 of the insulating channel members 25 envelop the edges 14 as well as the marginal portions 15 of the two faces of the cathode 10. Thus, the insulating channel members 25 function to mask the edges 14 of the cathode as well as the aforesaid marginal portions 15 of the faces of the cathode so that copper is not deposited at these edges, or on those portions of the cathode faces immediately adjacent to the edges. Furthermore, the V-groove 18 at the bottom edge of the cathode blank 10 causes the copper to deposit at this edge in the form of dendrites which develop in directions normal to the sides of the V-groove. The plane at which these dendrites meet in their growth is a plane of weakness at which the deposit can readily be broken. The cathode blank 10 may be formed of stainless steel, titanium, copper, a composite thereof in which stainless steel or titanium forms part or all of the surface, or other suitable corrosion resistant material.

The reusable cathode blank is made of relatively heavy gauge material having a thickness of about 0.1 inch to about 0.3 inch, e.g., 0.125 inch, thereby exhibiting substantial rigidity. This is in contrast with a typical cathode starting sheet which has a thickness of only about 0.026 inch or less. A stainless steel cathode blank having dimensions of 38 1/2 inches x 41 inches x 0.125 inch thick weighs about 68 pounds with the conductor bar affixed. With this relatively heavy structure, problems of establishing electrical contact to the busbars which had been experienced with light copper starting sheets are eliminated entirely since the heavy cathode blank

presses firmly at the contact points provided along the plating tank. Moreover the tenuous contact between the loops of the light sheet and the copper hanger bar are also eliminated.

The nature of the surface of the cathode blanks is such that the deposited copper is sufficiently adherent thereto, so as to support relatively heavy deposits of as much as several hundred pounds on a total surface area of from 8 to 25 square feet or more. On the other hand, the adherence of the deposited copper to the blanks is limited in that the copper can be stripped or peeled away from the blanks in two pieces without damaging the blanks. In the case of copper and stainless steel blanks it is advantageous to coat them with a parting medium to reduce adherence of the deposited copper. No such coating is required for titanium blanks.

It will be understood that a certain amount of handling and transportation of the cathode blanks is required in the plant incident to removal of the blanks from the electrolytic cell following the deposition step and prior to stripping. If the blanks were masked on the bottom edges as well as on the side edges, the vibrations resulting from such handling might well dislodge the deposited copper, which would be both hazardous and inconvenient. Thus, the combination of limited adherence of the deposited copper together with permitting the copper to deposit about the bottom edge of the cathode blanks, effectively prevents the deposited copper from falling during handling, while the plane of weakness in the bottom edge deposit eliminates any serious interference with the stripping operation.

In general, the finish of the cathode blank surfaces will influence the character of the adherence of the copper deposit to the cathode blank. A relatively rough finish on

the cathode blank will produce a more tenacious deposit than a relatively smooth finish. The surface roughness is measured in terms of microinches AA (arithmetic average) as determined by the Bendix Profilometer. It has been found that stainless steel blanks having a total surface area of 20 square feet and a surface roughness measuring between about 5 microinches AA and 110 microinches AA, e.g., 50 microinches AA, will support a copper deposit weighing in excess of 200 pounds, e.g., 220 pounds, and yet can be stripped from the blanks without undue effort and without damaging the blanks. Other cathode blank materials function similarly and, in general, surface finishes in the range of about 5 microinches AA to 110 microinches will be satisfactory.

The location and coverage of the edge masking is an important aspect of the invention. It will be noted that the edges of the cathode blank are substantially perpendicular to the main plane faces on which the copper is to be deposited. These edge faces are, by the very nature of the manufacturing process, e.g., shearing, necessarily imperfect to some extent. In addition to manufacturing imperfections, these edges will suffer nicking, denting and scratching in the ordinary day-to-day handling and stripping operations. During plating, these edge imperfections, if exposed, are completely filled by the copper which plates on all conductive surfaces. So long as the deposit is thin, i.e., equivalent to a thickness of the order of one to two days of plating, the deposited sheet may be sprung or forced off the blank. In doing so, of course there is some mechanical deformation of the sheet, but this is of little consequence because, in a regular deposition cell, the thin cathode starting sheet is straightened by manual

or mechanical means. However, when a heavy deposit of 1/4 inch or more in thickness is produced, it is essentially impractical to spring it free from the blank to which it is securely keyed by the edge imperfections. Further, when the cathode blank is removed from the electrolytic cell after deposition has been completed, the deposited copper cools rapidly and the resulting thermal contraction of the deposit on the blank causes the deposit to bind even more tightly. This latter condition is particularly severe when the coefficient of thermal expansion of the blank material is less than that of copper. Accordingly, it is important that the edge insulating masking members cover and insulate the entire side edge portions of the cathode blank. As a practical matter, to assure that the masking member is securely mounted and completely insulates the edge portions, the masking member will cover and insulate marginal portions of the cathode blank faces in addition to the side edges. A gasket positioned in a groove in the edge portion of the cathode member, as has been suggested in the prior art, is not suitable for use where heavy deposits of copper are required, because this structure leaves a portion of the side edge surface exposed for deposition of copper and is thus subject to the disadvantages described above.

The insulating masking members may be preformed from polypropylene or polytetrafluoroethylene or other non-water absorbant material. Instead of preformed insulation, an appropriate organic adhesive material, e.g., epoxy, may be brushed, sprayed, or otherwise applied to the area of the cathode which is to be insulated. One successful edge-masking system calls for wrapping the edge of the cathode with polytetrafluoroethylene tape and then shrink-fitting a polypropylene

preformed masking member over the tape.

The electrolyte used in electrolytic refining consists primarily of copper sulfate, introduced as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, and sulfuric acid. The copper content is usually from 2.8 to 3.5 per cent, by weight, corresponding to about 35 to 43 grams per liter of copper. Sulfuric acid is usually present in an amount of about 150 to 220 grams per liter.

10 The cathodes remain in the bath from 5 to 14 or more days at an operating temperature of about 40° to 60°C . and a current density of from 15 to 35 amperes per square foot. Deposits from $1/8$ to $3/8$ inch thick, having limited adherence to the cathode blank are formed on each side of the cathode, and the average weight of copper deposited on each cathode is not less than 5 pounds per square foot of surface area.

20 In stripping the deposits from the cathode blank, knives are inserted along the upper edge of the deposit, and the copper deposits on the faces of the cathode blank are separated from the blank along the edges of the insulating members. As the separating operation continues, the aforementioned plane of weakness in the deposit at the bottom edge of the cathode blank fails, and the two deposits on the faces of the cathode are thus separated. The cathode blanks may then be reused in an electrolytic cell for further copper deposition. Alternatively automated equipment using conveyors, rappers, suction devices, etc. may be used for stripping.

30 By way of example, stainless steel cathode blanks having the dimensions $38\frac{1}{2}$ inches wide, 41 inches long and about 0.125 inch thick were placed in a plating tank between crude copper anodes which were 36 inches wide, 36 inches long and $1\frac{1}{4}$ inch thick, weighed about 600 pounds and had a

copper content of about 99%. The distance between adjacent anodes and cathodes was 3 15/16 inches. The side edges of the cathode blanks were protected by shrink-fitted polypropylene insulating members which extended from the bottom edge of the cathode blank to a point on the cathode blank above the level of the electrolyte. The bottom edge of the cathode blanks had an inverted V-shaped groove therein. The electrolyte was composed of 40 grams per liter of copper and 200 grams per liter of sulfuric acid. The operating temperature of the bath was 147.4°F. A current density of 18.8 amperes per square foot was employed, and the current was passed for a period of 13.49 days. At the end of this period, the cathodes were removed from the electrolyte and the copper deposits thereon were stripped. The copper deposits had a thickness of about 5/16 inch and the total copper deposited on each of the cathodes averaged about 297 pounds in weight. The deposited copper was of a purity suitable for melting and casting into ingot, wire bar or other suitable shape. The electrodeposited copper stripped from the cathode blanks was washed completely clean of electrolyte since there were no loop crevices in which electrolyte could become entrapped as had been the case with electrolytic copper plated on copper starting sheets provided with contact loops. The condition of the cathode blanks was such that they were suitable for reuse in the process.

In applying the process of the invention to the field of electrowinning, the cathode starting sheets employed in the art heretofore are eliminated. Instead, heavy copper deposits are formed directly on masked, relatively rigid cathode blanks, of the type described above, over an extended period of time. The operation of the electrolytic cell in the

winning of copper from solutions, is in most respects similar to operation of such a cell in electrorefining of copper. However, a relatively insoluble but conductive anode is employed, and the source of the deposited copper is the electrolyte, which is rich in dissolved copper.

10 By way of example of the electrowinning of copper, a plurality of antimonial lead anodes which were 35 1/2 inches wide, 33 1/2 inches long and 1/2 inch thick, were positioned in an electrolytic cell. Between each pair of anodes was inserted a titanium cathode blank having submerged dimensions of about 37 1/2 inches wide, 37 1/2 inches long and 1/8 inch thick, and which had a surface roughness of about 50 to 100 microinches AA. The center to center distance between like electrodes was 4 1/4 inches. The side edges of the cathode blanks were protected by shrink-fitted polypropylene members which extended from the bottom edge of the cathode blank to a point on the cathode blank above the level of the electrolyte. The copper-rich electrolyte was composed on the average of about 70 grams per liter of copper and about 20 120 grams per liter of sulfuric acid. The operating temperature of the bath was about 45° to 50°C. A current density of about 30 amperes per square foot was employed, and the current was passed for a period of 7 days. During the operation of the electrolytic cell, electrolyte which was depleted in copper was continuously withdrawn from the cell. This effluent had the approximate composition of about 60 grams per liter of copper and about 135 grams per liter of sulfuric acid. At the end of the period, the cathodes were removed from the electrolyte and the copper deposits thereon were stripped. 30 These copper deposits had a thickness of about 1/4 to 5/16 inch

on each side of the cathode blank and the average total weight of copper deposited on each cathode was from about 200 to about 220 pounds. The deposited copper was of a purity suitable for melting or casting into ingot or wire bar or other suitable shape. The cathode blanks were substantially undamaged by the stripping operation and suitable for reuse in an electrolytic cell.

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Titanium cathode blanks have qualities which make them particularly beneficial in the copper deposition process which has been described. Thus, in addition to requiring no parting film, as mentioned above, since the copper does not adhere to the oxidized titanium surface, titanium is self-passivating if inadvertently made anodic, apparently almost completely corrosion resistant in the electrolyte employed, and, at least initially, the deposited copper has a finer grain structure than copper plated on other substrates. All of these items enhance the quality of copper produced.

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The process of the invention provides substantial cost savings as compared to prior practice using light electrolytic copper starting sheets having contact loops joined thereto. Labor costs attendant upon the preparation and tending of starting sheets are eliminated. The contact problem experienced with starting sheets has been solved, and the crevices, nodules and striations which held contaminating electrolyte under the starting sheet practice have been substantially reduced. Thus, the process provided in accordance with the invention not only eliminates a major cost factor, but also is much more trouble-free and leads to the production of higher quality copper.

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Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. In an electrolytic process for producing heavy deposits of high purity copper suitable for melting into ingot or wire bar form, wherein a plurality of cathodes and anodes are positioned in an electrolytic cell and immersed in an acid electrolyte containing dissolved copper, and wherein electric current is passed through the electrolyte to deposit copper upon the cathodes, the improvement comprising, the provision of relatively rigid plate-like reusable cathode blanks having a surface roughness of from 5 to 110 microinches AA, with each cathode blank having insulating masking means at at least the side edges thereof to prevent deposition of copper at and envelopment about the said edges, depositing copper for an extended period of time upon the exposed portion of said cathode blanks to secure limited adherence of said deposited copper to said cathode blanks, continuing deposition of copper until the deposited copper has a thickness of at least 1/8 inch on each side of said cathode blanks, stripping the deposited copper from the sides of the cathode blanks, and thereafter returning the cathode blanks to an electrolytic cell for further deposition of copper.

2. The electrolytic process of claim 1 wherein partially refined copper anodes are further refined by dissolution and deposition upon the cathode blanks, the anodes being substantially consumed in the process.

3. The process of claim 1 wherein each cathode blank is provided with an inverted V-shaped groove in the bottom peripheral edge thereof to promote the establishment of a plane

of weakness in the copper deposited at this edge, the deposition of copper being carried out for a period of from about 5 to 14 days at a current density of from about 15 to 35 amperes per square foot in an electrolyte at a temperature of from about 40°C. to 70°C., the electrolyte containing from about 30 to 100 grams per liter of copper, and from about 50 to 250 grams per liter of sulfuric acid.

4. The process of claim 3 wherein the cathode blanks are composed of a material selected from the group consisting of titanium, stainless steel, copper and composites thereof.

5. The process of claim 4 wherein the insulating masking means are formed of non-water absorbant materials.

6. The process of claim 5 wherein the insulating masking means are formed of polypropylene.

7. The process of claim 5 wherein the insulating masking means are formed at least in part of polytetrafluoroethylene.

8. The electrolytic process of claim 1 wherein the winning of copper from a copper-bearing solution is accomplished, the anodes being formed of a relatively insoluble conductive material and, during the process, removing copper-depleted electrolyte from the electrolytic cell and replenishing the remaining electrolyte with a copper-rich solution from an external source.

9. A relatively rigid plate-like reusable cathode blank adopted for the electrolytic deposition of copper thereupon, formed of a material selected from the group consisting of titanium, stainless steel, copper and composites thereof,

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a conductor bar at the top edge thereof to establish electrical contact, the side edges thereof being completely insulated from exposure to electrolyte and the bottom edge having an inverted V-groove therein to facilitate stripping the deposited copper, the cathode blank having a surface area characterized by a surface roughness of about 5 to 110 microinches AA whereby limited adherence of the deposited copper to the cathode blank surface is attained, the adherence between cathode blank and deposited copper being sufficient to support at least 5 pounds of copper per square foot of surface area while permitting the copper to be stripped after deposition is completed without damaging the cathode blank.



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